A Theory of the Deviation from Close Packing in Hexagonal Metal Crystals*

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A mechanism is proposed to show how the Fermi surface interacts with the Brillouin zone boundaries. The direction and relative magnitude of the variation of the c/a ratio for hexagonal crystals from the ideal value for close packing are predicted as a function of the electron-atom ratio, and these predictions are compared with values of lattice parameters which are reported in the literature.

I. INTRODUCTION

WHEN the metallurgist discusses crystal structure in metals, he usually thinks in terms of the packing of hard "spheres," and yet it is a long known fact that often the lattice axial ratio c/a shows variations from the value to be expected from this ideal model. The reason for these variations, at least at low temperatures, lies presumably in the origins of the cohesive binding energy of these metals since nature demands that the crystal assume that configuration which gives rise to a minimum crystal free energy or, at absolute zero, to a maximum cohesive binding energy. The customary cohesive energy calculation for metals is the cellular method of Wigner and Seitz.[1] In this method, however, one requires the one-electron wave functions which describe the valence electrons to be spherically symmetric about any nucleus. Bardeen[2] maintains this restriction in his correction for the effective mass of the binding electrons in the Fermi energy term. Unless an angular dependence is introduced into the valence electron wave functions, however, this method is unable to investigate how a variation in the axial ratio from the ideal value can lower the total free energy of the crystal.

Jones[3] has considered these distortions for the case of h.c.p. crystals with an electron-atom ratio, hereafter designated z in this paper, greater than 1.75, i.e., for the divalent metals and the ϵ- and η-phases of the β-brass type alloys. In these crystals the ideal axial ratio for the close-packing of "spheres" is $c/a = 1.633$. He argued that when the Fermi surface of the valence electrons overlaps a Brillouin zone boundary in a particular direction in reciprocal space, the electrons with wave numbers corresponding to the overlapping region exert a force to expand the lattice in the corresponding direction in the lattice space. Jones took the zone shown in Fig. 3 as the first Brillouin zone for the h.c.p. lattice and therefore argued that since overlap must occur through the A faces when $z > 1.75$, the ϵ-phase ($c/a < 1.633$) is to be expected whereas for values of z

approaching two the η-phase ($c/a > 1.633$) may appear due to overlap through the B faces.

This explanation, if correct, is only applicable to metals and alloys whose electron-atom ratios are large enough for overlap to occur through at least one set of zone faces. There are, however, many hexagonal metals with low z whose axial ratios show similar variations from their ideal value. Barrett and Trautz[4] have reported a low temperature h.c.p. phase in lithium where $z = 1$. They found that lithium transforms martensitically from the b.c.c. phase to a f.c.c. phase if cold worked at low temperatures, or spontaneously to an h.c.p. phase with axial ratio[5] $c/a = 1.563$ at lower temperatures. Among the transition metals and rare earths there are many instances of h.c.p. structures all of which have axial ratios which are less than the ideal value 1.633. Due to a demotion of the outer s-electrons in the formation of the crystal lattice, the value of z in these metals is approximately one. Since the density of states in the unfilled d- or f-bands of these metals is much larger than that in the s-band, it is difficult to determine how the s electron-atom ratio is varying as these elements are alloyed with one another. Although there are no definitive experiments as to the variation of the axial ratio with z in these h.c.p. lattices with low z, one nevertheless wonders by what mechanism the axial ratio should be less than the ideal value for all the h.c.p. lattices with approximately one valence electron per atom. Since the Fermi surface is completely contained within the first Brillouin zone, Jones's ideas are not applicable.

Owen and Edmunds[6] have examined the ζ-phase of the silver-zinc system and found it to be complex hexagonal with an axial ratio which varies from 0.7450 to 0.7383 as z increases from 1.46 to 1.5. Since the surface of the Brillouin zone for this structure is not reached until $z = 1.56$, the variation in c/a with z cannot be explained by zone overlap.

Several alloys with z-values in the neighborhood of $\frac{3}{2}$ have h.c.p. structures. In Table I are listed some of the experimentally recorded axial ratios. It is at once noted

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[1] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); and E. Wigner, Phys. Rev. **46**, 1002 (1934).

[2] J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

[3] H. Jones, Proc. Roy. Soc. (London) **A147**, 396 (1934).

[4] C. S. Barrett and O. R. Trautz, Am. Inst. Mining Met. Engrs. **175**, 579 (1948).

[5] C. S. Barrett, *Phase Transformations in Solids* (John Wiley & Sons, Inc., New York, 1951), p. 343. Edited by R. Smoluchowski *et al.*

[6] E. A. Owen and I. G. Edmunds, J. Inst. Metals **63**, 291 (1938).

that there is a progressive contraction of the symmetry axis with increasing electron-atom ratio. For values of z in the range $1.2 \leq z \leq 1.4$ the axial ratio is greater than 1.633 and decreases relatively slowly with increasing z. The axial ratio continues to decrease continuously to values of $c/a < 1.633$ for $z > 1.4$. In this range of z, therefore, the crystal transforms continuously from an η-brass phase to an ϵ-brass phase as z increases. When h.c.p. alloys with z values approaching two change from the ϵ-brass phase to the η-brass phase, on the other hand, the phase change is discontinuous and a mixture of the two phases can appear simultaneously in the same lattice. Is it possible for the same mechanism to cause a continuous change from the η-brass to the ϵ-brass phase when $z = 1.4$ and a discontinuous change from the ϵ-brass to the η-brass phase for higher electron-atom ratios? Again Jones' ideas cannot apply, at least for values of $z < 1.4$, since any overlap of the A faces, according to his mechanism, would force a distortion to $c/a < 1.633$.

The seemingly anomalous value of c/a in the gold-mercury system has been reported by two independent investigators. Pabst[7] first reported a narrow, homogeneous h.c.p. β-phase about $z = 1.25$ with $c/a = 1.647$. He found that as z varied from 1.2 to 1.34, the axial ratio increased from 1.638 to a maximum value of 1.647 in the neighborhood of $z = 1.25$, and then decreased slowly to 1.645 at $z = 1.34$. Stenbeck,[8] on the other hand, reported a practically constant value of $c/a = 1.647$ for values of z from 1.19 to 1.33. He was unable to find the maximum value in the c/a ratio at $z = 1.25$ reported by Pabst. According to his measurement, the homogenous β-phase extends from $z = 1.21$ to $z = 1.27$. He was not able to detect any ordering in his sample.

Typical of the measurements on alloys which show a discontinuous change from an ϵ-brass to an η-brass phase at high values of z are those of Owen and Pickup[9] on the copper-zinc system. They found that as z varies from 1.76 to 1.87, the axial ratio of the ϵ-brass phase decreases linearly from 1.570–1.554, that as z varies from 1.87–1.91 the axial ratio remains constant, that in the range $1.91 \leq z \leq 1.96$ both the ϵ- and the η-phase are present, and that as z increases from 1.97 to 2.0, the axial ratio of the η-phase increases linearly from 1.804 to 1.856. It will be seen that the forces which are responsible for these distortions are considerably more complex than the simple considerations of Jones.

Hume-Rothery and Raynor[10] have pointed out three of the experimentally important factors in any consideration of crystal structure in metal alloys, $viz.$, size factor, electro-chemical factor, and electron-atom ratio.

[7] A. Pabst, Z. physik. Chem., **B3**, 443 (1929).
[8] S. Stenbeck, Z. anorg. u. allgem. Chem. **214**, 16 (1933).
[9] E. A. Owen and L. Pickup, Proc. Roy. Soc. (London) **A140**, 179 (1933).
[10] W. Hume-Rothery and G. V. Raynor, J. Inst. Metals **66**, 191 (1940).

TABLE I. Experimentally recorded axial ratios of some h.c.p. alloys.

Alloy	z	c/a
Ag Al	1.45–1.85	1.625–1.588[a, b]
Ag Cd	1.46–1.55	1.619–1.608[c]
Ag Sn	1.43–1.59	1.630–1.616[d]
Ag Hg	1.44–1.45	1.630–1.617[e]
Ag Sb	1.4 –1.64	1.634–1.617[f]
Cu Si	1.35–1.4	1.635–1.633[g]
Au Hg	1.21–1.25–1.27	{1.638–1.647–1.645[h] / 1.647–1.647–1.647[e] }

[a] A. Westgren and A. J. Bradley, Phil. Mag. **6**, 280 (1928).
[b] W. Hofman and K. E. Volk, Metallwirtschaft **15**, 699 (1936).
[c] H. Astrand and A. Westgren, Z. anorg. u. allgem. Chem. **175**, 90 (1928).
[d] Niel, Almin, and Westgren, Z. physik. Chem. **14**, 81 (1931).
[e] See reference 8.
[f] Westgren, Hagg, and Eriksson, Z. physik. Chem. **B6**, 40 (1929).
[g] A. G. H. Anderson, Trans. Am. Inst. Mining Met. Engrs. **137**, 334 (1940).
[h] See reference 7.

Recently Zener[11] has pointed out the importance of the d-shell electrons in determining crystal structure in the transition metals. This paper will be concerned with variations in the axial ratio which appear to be predominantly determined by the electron-atom ratio. The Bloch[12] model is employed to investigate how the valence electrons of metals and their alloys can force distortions in a lattice from the packing of "spheres" in order to increase the cohesive binding energy of the lattice. Those lattices which have axial ratios which differ from the ideal value as a result of an ordering of atoms of different size are omitted from the discussion.

II. GENERAL THEORY

In order to understand the role of the valence electrons in determining crystal structure or crystal distortion, it is necessary to have a knowledge of the various factors which contribute to the binding energy of the crystal. The calculation of the internal energy of a metal compared with the energy of the widely separated individual atoms which compose it is usually made in two steps. First, the energy of the lowest level of the valence electrons is computed by some method such as that of Wigner and Seitz, and then the whole energy of the electrons referred to this lowest level, the Fermi energy, is calculated. Though the energy of the lowest level is sensitive to changes in atomic volume, it is not very sensitive to changes in crystal structure for a given atomic volume. Fuchs[13] has shown that the difference in energy of the lowest level of the valency electrons between the b.c.c. and the f.c.c. structures having the atomic volume of copper is only 10^{-3} ev per atom. The calculated energy difference between the b.c.c. and f.c.c. phases for copper of 0.1 ev per atom is due to the interaction of the closed d-shells which just touch in the noble metals. In this paper the d-electron contributions are neglected except in so far as they

[11] C. Zener, Phys. Rev. **81**, 440 (1951).
[12] F. Bloch, Z. Physik **52**, 555 (1928).
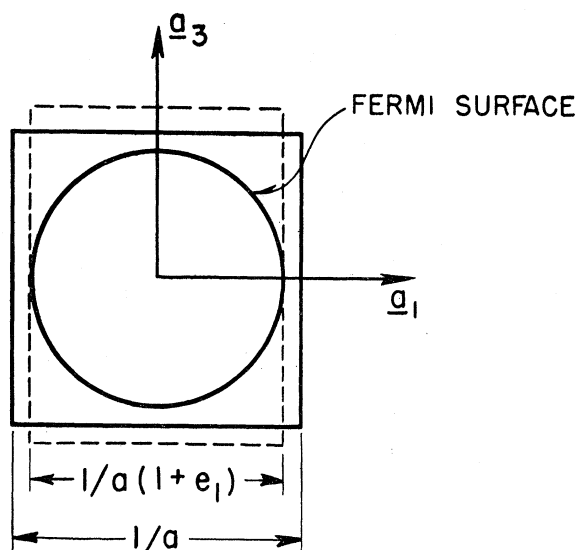[13] K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935).

FIG. 1. Brillouin zone for a two-dimensional square lattice before and after distortion.

contribute to the elastic constants of the metal or metal alloy. The Fermi energy, on the other hand, is sensitive to changes in structure even when the volume remains unchanged since the kinetic energy of the electrons which move in a periodic potential is not proportional to the square of the wave number, as in the case of free electrons, but depends upon the period of the lattice. It is assumed, therefore, that the lowest level of the valence electrons remains constant during a small distortion from the packing of "spheres" in any given phase. Consideration is given only to how changes in the Brillouin zone boundaries should effect the Fermi energy.

Brillouin[14] has shown that due to the perturbations inherent in the restrictions of a lattice on the otherwise freely moving electrons, the electron energy vs wave number curve in any direction in reciprocal space is not a parabola, as in the case of free electrons, but shows discontinuities at certain sets of planes in the lattice which are determined by the lattice configuration. The regions in reciprocal space which are enclosed by these energy discontinuity surfaces are the Brillouin zones of the lattice. When the crystal is subject to a shear which alters the lattice configuration, the positions of the Brillouin zone boundaries must also change. In order to study the effect of a change of shape alone on the binding energy of a crystal, only those distortions of the lattice which do not involve a volume change should be considered. If a crystal distorts without a volume change, then some of the Brillouin zone surfaces must move toward the center of the zone while others move away. In order to understand how the electron energy will change with movements of the energy discontinuity surfaces, consider a two-dimensional square

[14] L. Brillouin, $Quantenstatistik$ (Julius Springer, Berlin, 1931).

lattice. The Brillouin zone for this lattice is a square of side $1/a$, where a is the lattice parameter. Figure 2 (a) represents, schematically, the electron energy vs wave number curve for the direction a_1 of Fig. 1 and Fig. 2 (b) the electron energy vs wave number curve for the direction a_3. If the lattice is given a positive strain e_1 and a negative strain e_3 subject to the constraint $(1+e_1)(1+e_3) = 1$, then the Brillouin zone will shear in the opposite direction as shown in Fig. 1. This means that the wave number corresponding to the surface of energy discontinuity will move to smaller absolute values in the a_1 direction and larger absolute values in the a_3 direction as shown in Fig. 2. Since the crystal volume remains constant during the distortion, the density of energy states in k-space remains constant. The Fermi surface will, therefore, remain stationary through the distortion if no redistribution of electrons takes place and if it does not intersect a zone boundary. A redistribution of the electrons will cause the Fermi surface to bulge slightly in the direction of the approaching surfaces.

It is now apparent that if the Fermi surface is close to but does not yet intersect or touch a particular energy discontinuity surface, a movement of that surface towards the Fermi surface, as in Fig. 2 (a), will lower the average electron energy due to the shift in the position of the energy gap. The Fermi surface exerts, as it were, a force of attraction on the energy discontinuity surface. This force will be greater the larger the energy discontinuity across the surface, the smaller their distance of separation, and the larger the energy of the Fermi surface. The last dependence results from the fact that the larger the energy of the Fermi surface, the smaller the curvature of the surface and therefore the larger the area of Fermi surface within a given distance from the energy discontinuity surface. The energy levels which are most affected by the movement of the Brillouin surface correspond to those values of k in the immediate neighborhood of the surface. Therefore, as the Fermi surface of a crystal approaches, as the electron-atom ratio is increased, the surface of a Brillouin zone, there will be an increasing opportunity for the crystal to lower its average electron energy by a distortion which will cause the zone surface to move in the direction of the closest element of area of the Fermi surface. Since the Fermi surface, before it intersects any boundaries, is approximately spherical, this direction of motion will be normal to the zone surface toward the center of the zone.

If the electron-atom ratio is so large that the Fermi surface intersects the Brillouin zone surface, any movement of the zone surface toward the center of the zone will result in two opposing energy changes. There will be a decrease in the energy vs wave number surface due to the change of position of the energy gap which will tend to lower the average electron energy. There will also, however, be an increase in the energy of the Fermi surface due to a redistribution of the electrons which are displaced by the movement to unoccupied energy

states. This latter effect, which will tend to increase the average electron energy, will begin abruptly so that the force of attraction between the Fermi surface and the energy discontinuity surface should show a sharp maximum at that value of z for which the two surfaces just touch. If the energy discontinuity across the Brillouin zone surface is large so that overlap of the zone surface does not take place, the repulsive force between the two surfaces may dominate as z is increased further so that the Fermi surface now pushes the energy discontinuity surface away from the center of the Brillouin zone.

When the Fermi surface begins to overlap the energy discontinuity surface, the repulsive force between the two surfaces will be partially relieved since not all of the electrons which are displaced by a movement of the energy discontinuity surface toward the center of the zone are forced to energy states which increase the energy of the Fermi surface. Some of the displaced electrons are forced to energy states which, though greater in energy by the magnitude of the energy gap, are still of lower energy than the Fermi surface. Although the total force between the Fermi and Brillouin surfaces may be repulsive, the decrease in the repulsive force between the two surfaces because of zone face overlap can be considered to contribute an effective partial pressure against the zone boundary to push it toward the center of the zone. This partial pressure will begin abruptly at that value of z for which overlap of the Brillouin zone surface begins.

Finally it should be noted that when there is complete overlap of an energy discontinuity surface, a movement of this surface toward or away from the center of the Brillouin zone will have little effect on the average valence electron energy. The perturbation of the electron energy vs wave number curve in any direction through the energy discontinuity surface is of equal magnitude on either side of the surface. The average electron energy, when the perturbed states on each side of the energy discontinuity are included, is therefore the same as it would be were there no surface of energy discontinuity present.

We can qualitatively conclude, therefore, that as the Fermi surface of a metal approaches, with increasing z, a Brillouin zone energy discontinuity surface, there will be a force of attraction between the two surfaces. Once the Fermi surface intersects an energy discontinuity surface, there will be two opposing forces between the surfaces. The repulsive force between the two surfaces will increase with increasing intersection of the surfaces, or with increasing z. The rate of increase with z of this repulsive force will decrease when overlap of the zone surface by the Fermi surface begins as a result of what may be thought of as a partial pressure of the overlapping electrons to push the Brillouin zone surface toward the center of the zone. The maximum repulsive force between the two surfaces should occur at that z for which the low energy side of the energy discon-

tinuity surface is just completely intercepted by the Fermi surface, since the number of electrons which are displaced by a movement of the zone surface cannot increase for larger values of z whereas the partial pressure due to the overlapping electrons does increase. If the electron-atom ratio is increased beyond this, therefore, the total force on the energy discontinuity surface will decrease toward zero.

Any Brillouin zone is composed of several energy discontinuity surfaces of different orientation, and there will be similar forces of interaction between each of these faces and the Fermi surface. From Fig. 1 it is apparent that if the Fermi surface exerts a force of attraction on all the Brillouin zone surfaces, then though some of the faces will move in the direction of the attractive force in a constant volume deformation, the other faces will be forced to move against this force. There results a competition among the zone faces for movement toward the center of the zone. The type of distortion to be expected in a crystal will therefore depend upon the relative magnitudes of the forces between the Fermi surface and the various energy discontinuity surfaces. In cubic crystals the Brillouin zones are composed of families of energy discontinuity surfaces which are symmetrical with respect to the origin in reciprocal space and therefore equidistant from the Fermi surface.
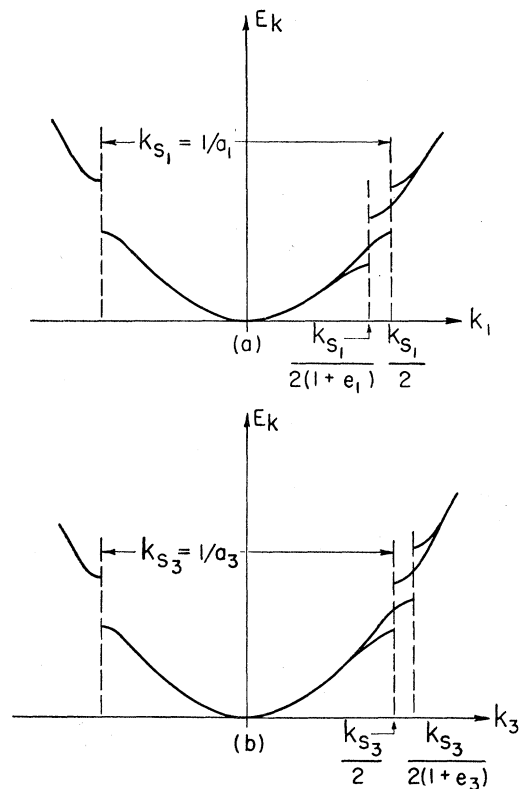

FIG. 2. Schematic representation of variations in the electron energy vs wave number curves for different directions in a metal lattice under strain.

The energy gap across each equivalent face is the same, and therefore each equivalent face is subject to an identical force of attraction toward or repulsion from the center of the zone. Since the restoring forces possess the same cubic symmetry in a cubic lattice, there is no preferred direction of shear as a result of the force of interaction between the Brillouin zone surfaces and the Fermi surface. Also, since the equivalent Brillouin surfaces in cubic crystals are sets of $\{n, n, m\}$ planes, the linear coefficients of the strains in the expression for the change of average electron energy due to a movement of each equivalent face are the same. If, therefore, the distortion is without a volume change, the resulting restraint on the strains will cause the linear term to vanish in the expression for the total change in the average electron energy with distortion. Any contribution to the energy change with distortion due to a redistribution of the electrons among the energy states will also be of second order in the strains, since both the number of electrons which would redistribute themselves and the amount of energy change of each in any redistribution are proportional to the strains. In cubic crystals, therefore, any increase in binding energy with distortion due to the "electron energy anisotropy"
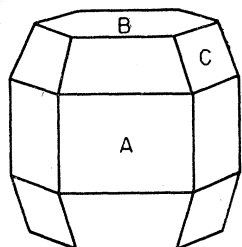

Fig. 3. First Brillouin zone for the h.c.p. lattice. It is bounded by the 20 planes $\{1\bar{1}0, 0\}$, $\{1\bar{1}0, 1\}$, $\{000, 2\}$.

effect, to name the mechanism under discussion, can be only a second-order effect. Nevertheless, this effect should be considered in any quantitative calculation of the elastic constants in cubic crystals since here one is interested in the second derivative of the energy change with respect to the strains.

When the lattice structure is noncubic, however, the "electron energy anisotropy" effect is a first-order effect, and the directions of the resulting distortions of the lattice should be predictable. In the hexagonal lattices, for example, the sets of Brillouin zone faces parallel to the symmetry axis will be reached by the Fermi surface, as it expands with increasing electron-atom ratio, at a different time than the faces perpendicular to the axis or sets of faces intersecting the axis at acute angles so that there is an uneven competition for contraction perpendicular and parallel to the axis. There results a decrease in the average electron energy with distortion which is to the first order in the strains whereas the restoring force is to the second order in the strains, and distortions of the lattice result.

As is evident from the discussion of the single energy discontinuity surface, not only is the shape of the

Brillouin zone an important factor in determining distortion to tetragonality in crystals, but also its fullness, or the electron-atom ratio z. If the zone is nearly empty so that only those energy states are occupied which are closely proportional to the square of the wave number, there will be practically no change in the Fermi energy as a result of a constant volume lattice distortion. The curvature of the electron energy vs wave number surface which pertains to the occupied energy states is not appreciably altered, and the electrons are free to minimize their kinetic energy by a redistribution among the energy states. If z is increased so that the Fermi surface approaches the set of equivalent energy discontinuity planes closest to the center of the Brillouin zone, the Fermi surface will exert an increasing force of attraction on the zone surfaces. In crystals with hexagonal symmetry all the bounding surfaces of an equivalent set cooperate to cause a similar distortion parallel to the symmetry axis as they respond to the attractive force of the Fermi surface. The crystal will therefore prefer to suffer a shear in which the nearest set of zone surfaces move closer to the center of the zone. For values of z such that the Fermi surface intersects the nearest set of cooperating faces but has not yet reached the competing set of zone surfaces, the crystal may prefer to shear in the opposite direction. If z is further increased, the relative magnitudes of the various competing forces will determine the direction of crystal shear.

III. BRILLOUIN ZONE CONSIDERATIONS

Before the general considerations just discussed are applied to the particular examples of distortion in metals and metal-alloys which were previously cited, it is necessary to first examine the Brillouin zones for the h.c.p. lattice and for the ζ-phase of the silver-zinc system. It will also be instructive to consider briefly the zone for the f.c.c. lattice.

In Fig. 3 is shown the first Brillouin zone for the h.c.p. lattice.[15] The number of energy states per atom included within a Brillouin zone, according to the Pauli principle and the periodic boundary conditions for the Bloch electronic wave function, is given by twice the product of the atomic volume and the Brillouin zone volume. The number of energy states per atom in the first zone of the ideal h.c.p. lattice is, therefore, 1.75. In Fig. 4 is pictured the zone for the h.c.p. lattice which just contains two energy states per atom. Consider now what might be expected to happen as these zones are filled up by an increase of the electron atom ratio z. It is assumed, for convenience, that the Fermi surface is a sphere. This is a good approximation only when the first zone is partially filled. It will, however, serve as a first approximation. If there were no distortion from the close-packing of hard spheres, i.e., if $c/a = 1.633$, and if there were no energy discontinuity across the zone surfaces, then the Fermi surface would just touch the

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[15] Refer to Appendix I

surface A when $z_A = (2\pi/9)(c/a) = 1.14$, the surface B when $z_B = (2\pi/\sqrt{3})(a/c)^2 = 1.36$, and the surface C when $z_C = (2\pi/9)(c/a)\{1+\frac{3}{4}(a/c)^2\}^{\frac{1}{2}} = 1.67$. If the magnitude of the energy discontinuity across face A is 1 ev when the lattice parameter is $a = 3A$, then overlap of the A faces will occur when $z_A' = 1.45$, and the Fermi surface will just touch the respective zone surfaces when $z_A = 1.14$, $z_B = 1.32$, $z_C = 1.57$. If an h.c.p. lattice has $c/a = 1.633$ when $z = 0$ and z is increased, then as z approaches 1.14 there will be an increasing tendency for the lattice to distort in such a way that the zone surfaces A are brought closer to the center of the zone. The average electron energy is lowered if electrons occupy the energy states which are depressed by the perturbation in the vicinity of the zone surfaces. Such a distortion would decrease the c/a ratio found in the real lattice. Since the two B faces, which would favor a distortion in the opposite sense, are farther from the center of the zone than are the A faces, and since there are only two B faces compared with six A faces, their competing influence will be smaller than that of the A faces provided the energy gaps of the two sets of zone faces are of similar magnitude. It is concluded, therefore, that when $z \leq 1.14$, the valence electron pressure for distortion in h.c.p. crystals is in such a direction as to favor $c/a < 1.633$. The change in valence electron energy will be to the first order in the lattice strains while the restoring force is of second order so that a finite distortion should take place. Although the maximum distorting force before distortion will be at $z = 1.14$, the maximum distortion should occur at that z for which the distorting force is a maximum after distortion. For a distortion to $c/a = 1.563$, the Fermi surface will just touch the A faces when $z_A = 1.09$.

If $z = 1.32$, there is sufficient intersection of the A faces by the Fermi surface for the repulsive force between these surfaces to nearly overbalance the attractive force. The B faces, on the other hand, will be experiencing a maximum force of attraction toward the center of the zone. The net interaction between the Fermi surface and the A and B faces, therefore, would produce a distortion to a $c/a > 1.633$. Because there are only two B faces, the maximum attractive force between the Fermi surface and the B faces will be smaller than that between the Fermi surface and the six A faces if the energy discontinuities across these faces are of similar magnitude. There will also be an attractive force between the Fermi surface and the twelve C faces which will work against a distortion to $c/a > 1.633$. If, therefore, a distortion to $c/a > 1.633$ occurs for values of z in the neighborhood of 1.32, it should be small compared to the maximum distortions to $c/a < 1.633$ at other z values.

Since only half of any C face will be interacting with the Fermi surface if A face overlap has not yet begun, and since the angle with which these surfaces intersect the symmetry axis is defined by $\tan\theta = (\sqrt{3}/2)(a/c)$, the total effect of the C faces will be roughly the same as 2.6

C faces parallel to the symmetry axis at the same distance from the center of the zone. As z increases beyond 1.32, the attractive forces acting on the C faces will be increasing rapidly along with the repulsive component of the interaction force on the B faces. These increases will be counterbalanced by the increase of repulsive force on the A faces before A face overlap begins. A slow variation in the total shearing force with z in the region $1.3 \leq z \leq 1.45$ should not, therefore, be surprising. According to the simple model of a spherical Fermi surface, the maximum attractive force acting on


FIG. 4. The Brillouin zone for the h.c.p. lattice which contains just two valence electrons per atom. It is bounded by the planes $\{1\bar{1}0, 0\}$, $\{1\bar{1}0, 1\}$, $\{000, 2\}$.
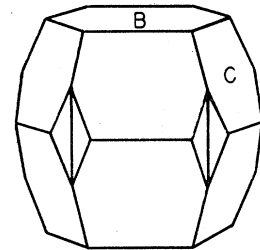
the B faces after a distortion to $c/a = 1.647$ will occur at a $z_B = 1.29$.

After A face overlap occurs, the rate of increase with z of the repulsive force on the A faces will diminish while that on the B faces will increase. The increasing attractive force between the Fermi surface and the twelve C faces will therefore cause the axial ratio for any given alloy to decrease continuously with increasing z. Since the Fermi surface will not reach both halves of a C face at the same time because of the energy discontinuity across the A faces, there will be a broad maximum in the attractive force between the Fermi and zone

FIG. 5. First Brillouin zone for the f.c.c. lattice.
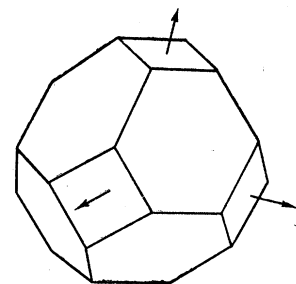
surfaces in the range $1.6 < z < 1.8$. The axial ratio will, however, continue to decrease in this range due to the increasing force of repulsion on the B faces. The actual rate of variation will depend upon the elastic constants of the particular alloy, the magnitude of the respective energy discontinuities, and the atomic volume. Figure 9 shows how the various contributions of the different faces to the total shearing force combine.

For values of z close to two, the A faces will be largely overlapped so that their interaction with the Fermi surface will be relatively small. The repulsive forces

between the Fermi surface and the B and C faces will predominate. If no overlap of the zone boundaries takes place, the repulsive forces will make the zone of Fig. 4 as "round" as possible so as to lower the energy of the Fermi surface. This means that the shearing force due to the repulsive forces will vanish if the B faces are equidistant with the C faces from the center of the zone. This occurs only if there is a distortion to $c/a < 1.633$. In fact, $k_B = k_C$ when $c/a = 1.50$. If there is no overlap, therefore, there will be a force to shear the crystal to an axial ratio $c/a = 1.50$. Since this force will decrease with the distortion while the reactive forces which resist distortion increase with the strains, the maximum distortion to be anticipated in any divalent h.c.p. metal should be about midway between these extremes, or to a $c/a \cong 1.56$. If, on the other hand, B face overlap does take place, then the repulsive force on the B face will be reduced by the effective partial pressure of the overlapping electrons. If B face overlap is occurring, however, the repulsive force on the C faces will continue to increase rapidly with increasing z. There may, therefore, be some value of z for which the repulsive forces on the C faces will predominate so that distortions to $c/a > 1.633$ result. Since the repulsive force on the twelve C faces
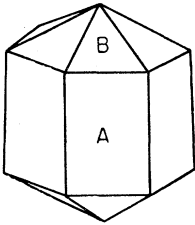

Fig. 6. Probable first Brillouin zone for the complex h.c.p. ζ-phase of the silver-zinc system.

will increase rapidly with small changes in z near to two, a gradual change from the ϵ- to the η-brass phase cannot occur. The crystal will be at a lower energy if it forms two distorted phases than if it forms one homogeneous phase with no distortion. The reason for the continuous change of axial ratio in the neighborhood of $z = 1.4$ would appear to be the slowness of the variation in the total distorting forces in the transition region from one phase to another and the smallness of the maximum force distorting the crystal to axial ratios greater than 1.633. If z is close to two and the zone is nearly full, the interface between the Fermi surface and the twelve C faces comprises a large fraction of the total Fermi surface. Any displacement of the C faces towards the center of the zone, therefore, displaces a large number of electrons while the available non-intersecting Fermi surface to which they may be displaced is small. There results a large change in the energy of the non-intersecting Fermi surface with a small change in the position of the C faces. The respulsive force between the Fermi surface and the twelve C faces increases rapidly, therefore, with z approaching two. If the electron-atom ratio is so large that only the η-brass phase is present, the

axial ratio should increase rapidly with increasing z due to the increasing force of repulsion on the C faces. These features of the h.c.p. lattice are summarized in Fig. 9.

In Fig. 5 is shown the form of the first Brillouin zone for the f.c.c. lattice. The number of states in the inscribed sphere of this zone is $\sqrt{3}\pi/4 = 1.36$. It is therefore expected that as z approaches 1.36, there will be a decrease in the stability of the cubic configuration and an increasing likelihood that a f.c.tet. phase appear. Due to the symmetry of the zone structure, there is no preferred axis for elongation. Also the eight faces which are met when $z = 1.36$ compete equally for opposing distortions so that any lattice shear will only be accompanied by a decrease in the valence electron energy which is of second order smallness. Therefore, although alloys with a f.c.c. structure with $z \cong 1.36$ are in the optimum range for distortion to tetragonality, it is not surprising that there are no known instances of f.c.tet. crystals as a result of the interaction of the valence electrons with the crystal lattice.

Consider, finally, the complex h.c.p. ζ-phase of the silver zinc system. Owen and Edmunds[6] have proposed an hexagonal structure for this phase with 54 atoms to the unit cell. For an electron-atom ratio of 1.48, they give values of c and a of 5.646A and 7.615A, respectively, or an axial ratio $c/a = 0.742$. To construct the probable first Brillouin zone for this phase, note that if k_0 is the radius in k space of the Fermi sphere corresponding to z electrons per atom and Ω is the atomic volume, then

$$k_0 \doteq [(3/4\pi) \cdot (z/2\Omega)]^{\frac{1}{3}} = 0.224 \text{A}^{-1},$$

for the values quoted above for which x-ray data was published. The x-ray measurements showed two lines of very strong intensity corresponding to the hexagonal Miller indices (3, 0, 0) and (2, 0, 2). Since the distance between parallel reflection planes in the hexagonal lattice is given by

$$d = \{(4/3a^2)(h^2 + k^2 + hk) + l^2/c^2\}^{-\frac{1}{2}},$$

the two very strong lines appear to be composed of overlapping reflections from the set of six $\{3\bar{3}0, 0\}$ and the set of twelve $\{2\bar{2}0, 2\}$ planes which are at distances from the origin in k-space of 0.228A^{-1} and 0.233A^{-1}, respectively. These two sets of planes form the zone shown in Fig. 6. For an axial ratio $c/a = 0.742$, the Fermi sphere will just touch the zone surfaces marked A in Fig. 6 when $z = 1.56$ and the zone surfaces B when $z = 1.67$. If the Fermi surface does not intersect any of the zone boundaries, the force of attraction on the A faces favors a contraction in reciprocal space perpendicular to the symmetry axis, or a decrease in the axial ratio c/a, while the force of attraction on the B faces, since they intersect the symmetry axis at an angle $\theta > 45°$, favors an opposite distortion. Since the A faces exert their maximum influence when $z = 1.56$ and the B faces when $z = 1.67$, it is predicted that as z

approaches the value 1.50, the c/a ratio will decrease with increasing z.

IV. ORDERS OF MAGNITUDE

The average energy per atom of the valence electrons whose wave numbers are defined by any volume Ω_k of k space is

$$U = 2\Omega \int_{\Omega_k} E_k d^3\mathbf{k}, \tag{1}$$

where Ω is the atomic volume of the metal. If z is the number of electrons per atom which have wave numbers within the volume Ω_k, then

$$z = 2\Omega \int_{\Omega_k} d^3\mathbf{k}. \tag{2}$$

Since the number of valence electrons remains constant during a distortion of the lattice, $\partial z/\partial e = 0$, where e is the lattice strain, and

$$\partial U/\partial e = -z' E_k{}^f(\tfrac{1}{2}k_s)\{\alpha - \beta + \gamma\}, \tag{3}$$

where $z' = 2\Omega \cdot (4\pi/3)k_0{}^3$, $E_k{}^f(k) = \hbar^2 k^2/2m$, and α, β, γ are dimensionless parameters. The parameters α and β have been calculated for the simple model of Fig. 7.[16]

With $\mu = k_s/2k_0$, $Q = |V_s|/2E_k{}^f(\tfrac{1}{2}k_s)$, and $\cos^{-1}\lambda$ the angle between the normal to a Brillouin zone surface and the line joining the center of the zone to the mean edge of that surface, the calculation gives $\alpha = \alpha(\lambda, \mu, Q)$ arising from the attractive force between the two surfaces and $\beta = \beta(\mu, Q)$ from the repulsive force between the two surfaces if they intersect one another. $\beta = 0$ if $\mu \geq 1$. The dimensionless parameter γ is zero unless there is zone overlap. If the valence electrons see a coulombic potential about each lattice site, $|V_s| \propto 1/k_s{}^2$ and

$$\partial |V_s|/\partial e = -k_s \partial |V_s|/\partial k_s = 2|V_s|. \tag{4}$$

Although there is, therefore, an increase of the energy gap with contraction of a zone surface to decrease γ, the parameter will nevertheless be positive.

For all three sets of faces in the h.c.p. lattice, the parameter λ is nearly $\sqrt{3}/2$. In Fig. 8 the dimensionless coefficient α is plotted as a function of Q. The attractive force between the Fermi energy and the Brillouin zone surface increases rapidly for larger Q, or for larger energy discontinuities. If the energy gap across the A faces is $2|V_s| = 1$ ev, then $Q = 0.005a^2$ where a is the lattice parameter in Angstrom units.
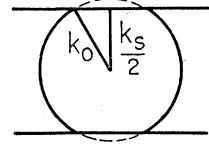
If σ is the stress in dynes per square centimeter producing the strain e, then

$$\sigma = -\frac{1}{\Omega}\frac{\partial U}{\partial e} = \frac{1}{\Omega} \cdot z' E_k{}^f\left(\frac{k_s}{2}\right)\{\alpha - \beta + \gamma\}. \tag{5}$$

In the case of a uniform lateral stress acting in all

[16] Refer to Appendix II.

FIG. 7. Cross section of Fermi sphere intersecting pair of Brillouin zone surfaces.

directions at right angles to the z axis,

$$\sigma_1 = -\frac{1}{\Omega}\frac{\partial U}{\partial e_A},$$

where $(1 + e_A) = (1 + e_1)^2 \cong 1 + 2e_1$, and therefore the strain e_1 to be expected in an h.c.p. crystal is

$$e_1 = \frac{1}{2\Omega}(S_{11} + S_{12})z' \sum_{(1)} E_k{}^f\left(\frac{k_s}{2}\right)\{\alpha - \beta + \gamma\}$$

$$+ \frac{1}{\Omega}S_{13}z' \sum_{(3)} E_k{}^f\left(\frac{k_s}{2}\right)\{\alpha - \beta + \gamma\},$$

where the first summation is taken over all pairs of faces which contribute to stresses perpendicular to the symmetry axis and the second summation refers to all pairs of faces which contribute to stresses parallel to the symmetry axis. The S_{ij} are the elastic constants of the metal. Since all of the elastic constants for hexagonal crystals are not customarily known, Young's modulus E is used to give an order of magnitude estimate. In Fig. 9 is plotted

$$2\Omega E_1 e_1 \cong z'\left[\sum_{(1)} E_k{}^f(\tfrac{1}{2}k_s)\{\alpha - \beta + \gamma\} - \sum_{(3)} E_k{}^f(\tfrac{1}{2}k_s)\{\alpha - \beta + \gamma\}\right] \tag{6}$$

as a function of z under the assumption that $a = 3A$ and $Q_A = 0.05$, $Q_B = 0.08$, $Q_C = 0.06$ where Q_i refers to the ith face. This gives a qualitative picture of the expected variation of the strain e_1 with z for a given crystal. The choice of $Q_A = 0.05$ is arbitrary. It represents an energy
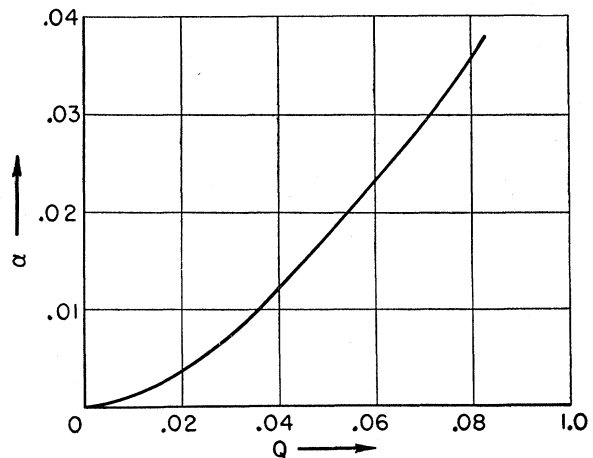

FIG. 8. Variation of α with $Q = |V_s|/2E_k{}^f(\tfrac{1}{2}k_s)$ for a pair of zone surfaces when $\mu = 1$, $\lambda = \lambda' = \tfrac{1}{2}\sqrt{3}$.
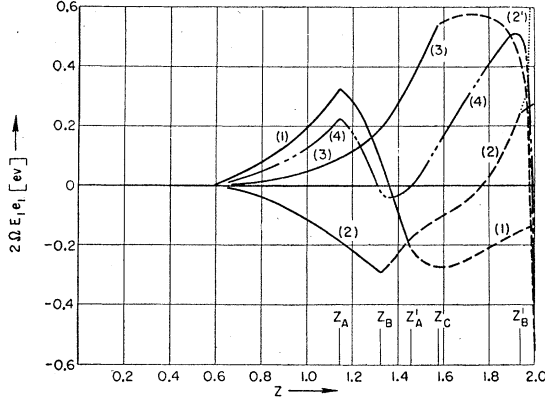
FIG. 9. Contributions to initial electron energy change per atom with strain in h.c.p. lattice with $a=3A$ for distortions to $c/a<1.633$ by (1) A faces; (2) B faces; (3) C faces. (4) is the resultant contribution. The solid curves are calculated from Eq. (6) with $Q_A=0.05$, $Q_B=0.08$, $Q_C=0.06$. The dashed lines are conjectured extrapolations. (2′) is conjectured B face contribution if there is no B face overlap.

gap of $10/a^2$ ev across the A faces if a is expressed in Angstrom units. Since,[17] however, the energy discontinuity can be expressed in terms of the nuclear charge Z, the atomic scattering factor F_s, and the structure amplitude S_s as

$$2|V_s| = \frac{2e^2}{\pi\Omega|k_s|^2}\{Z-F_s\}S_s, \qquad (7)$$

and since $E_{k'}(\frac{1}{2}k_s)\propto k_s^2$, the Q_i's should be in the approximate ratio

$$Q_A:Q_B:Q_C = \frac{S_{100}(Z-F_{100})}{k_A^4} : \frac{S_{002}(Z-F_{002})}{k_B^4} : \frac{S_{101}(Z-F_{101})}{k_C^4}$$

$$\cong 1:1.6:1.2.$$

The expression for α breaks down for large values of z where the Fermi surface is intersecting most of the Brillouin surface. The curves are therefore only qualitatively extrapolated for these larger z values. The relatively broad maximum for the C face contribution arises from the fact that the Fermi surface does not reach both halves of the C faces at the same time, that part of the C face which bounds the second zone being reached at a greater z-value.

V. COMPARISON WITH EXPERIMENT

The axial ratio for the h.c.p. lattice which is distorted from the ideal packing of spheres by a strain e_1 perpendicular to the symmetry axis is

$$c/a = 1.633/(1+e_1)^3.$$

From Fig. 9 it is apparent that e_1 is positive for values of $z<1.14$ and therefore that the transition and rare-earth metals which have h.c.p. structures should have

[17] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1936), p. 78.

a $c/a<1.633$. The actual value of the valence electron-atom ratio in these elements is difficult to determine due to an uncertainty in the amount of demotion of the s-electrons to the d- or f-shell. Measurements of the saturation magnetization of cobalt, however, indicate that this element has 0.7 valence electrons per atom. Since $E_1=2.07\times10^{12}$ dynes/cm^2 and $2\Omega=22\times10^{-24}$ cm^3, if $Q_A=0.05$, $Q_B=0.08$, $Q_C=0.06$, then $e_1=0.001$ and the axial ratio for cobalt should be $c/a=1.628$. The experimentally measured value for the axial ratio is 1.623, a value corresponding to $e_1=0.002$. It should be noted that if one wanted to use a knowledge of the axial ratio and elastic constants to estimate the number of valence electrons in the metal, it would be necessary to know the magnitude of the energy discontinuity across the various faces.

In the case of the low temperature h.c.p. phase of lithium, $z=1$ and $2\Omega=40\times10^{-24}$ cm^3. If $E_1=0.5\times10^{12}$ dynes/cm^2 and $Q_A=0.05$, $Q_B=0.08$, $Q_C=0.06$ are assumed to be the appropriate values for the lithium h.c.p. structure, then $e_1=0.013$ and $c/a=1.570$ as against the experimentally reported value 1.563. It appears, therefore, that the "electron energy anisotropy" effect is of sufficient magnitude to cause the observed distortions from the ideal packing of "spheres" in hexagonal crystals.

Figure 9 also predicts that $e_1<0$ if $1.29\leq z\leq1.46$. The exact range of z for which $e_1<0$ and the magnitude of e_1 depend upon an arbitrary assignment of the magnitude of the energy discontinuities across the various Brillouin zone surfaces. There are three qualitative features which are important, however. First, there is the existence of a range of z for which $c/a>1.633$; second, the magnitude of the maximum distortions to $c/a>1.633$ in this range should be smaller than the maximum distortions to $c/a<1.633$ on either side of this range; and third, the rate of change of distortion with z in this range should be small. From Table I it is observed that experimentally one finds distortions to $c/a>1.633$ which are small in magnitude and vary slowly with z in the range $1.21\leq z\leq1.4$. Pabst[7] has even reported observation of a maximum in the axial ratio at $z=1.25$ in the gold-mercury system. The qualitative features of Fig. 9 for $1.29\leq z\leq1.45$ are in general accord with the observed variations of the axial ratio with electron-atom ratio. Whereas the qualitative curve predicts a maximum axial ratio for $z=1.29$ when $c/a=1.647$, the observed maximum appears to be at about $z=1.25$, a discrepancy which could well be due to the simplified model of a spherical Fermi surface.

Figure 10 indicates how the "electron energy anisotropy" effect is dependent upon the magnitude of the energy gaps and the lattice parameter. The ratio $Q_A:Q_B:Q_C$ is held constant. If the lattice parameter is fixed and the energy gaps are increased, the magnitude of the maximum distortion to $c/a>1.633$ is decreased while the z-value at which it occurs is increased. For fixed energy gaps $c/a>1.633$ occurs for a lower range of

z-values and has a larger maximum value if the lattice parameter is decreased.

The qualitative arguments of the interaction of the Fermi surface with all of the zone faces also predict a nearly linear decrease in the axial ratio with z in the range $1.45 \leq z \leq 1.85$ in agreement with measurements given in Table I and those of Owen and Pickup[9] on ϵ-brass. They also show the possibility of a phase change to the η-brass phase for values of z close to two if there is sufficient B-face overlap.

Finally, consider the complex h.c.p. ζ-phase in the silver-zinc system. This phase also has a single symmetry axis so that the variations with z in the axial ratio should be predictable. It was predicted in the general discussion of the Brillouin zone for this phase that as z increased towards 1.50, the c/a of the crystal should decrease. This is in agreement with the measurements of Owen and Edmunds.[6]

VI. SUMMARY

In summary, a mechanism has been considered whereby the valence electrons in hexagonal metallic crystals can influence the lattice structure due to a change in their average energy with variation of the lattice axial ratio. It was shown how the Fermi surface for the metallic binding electrons interacts with surfaces of energy discontinuity which constitute the Brillouin zone boundaries. Before the Fermi surface reaches the energy discontinuity surface, there exists a force of attraction between them which depends upon their distance of separation, the magnitude of the energy discontinuity across the zone surface, and the energy of the Fermi surface. If the two surfaces intersect one another but do not overlap, there is also a repulsive force between the two surfaces which depends upon the area of interface between the two surfaces and the area of Fermi surface which is not a common interface with some other zone boundary. After overlap of a zone boundary by the Fermi surface, the amount of unoverlapped interface no longer increases so rapidly
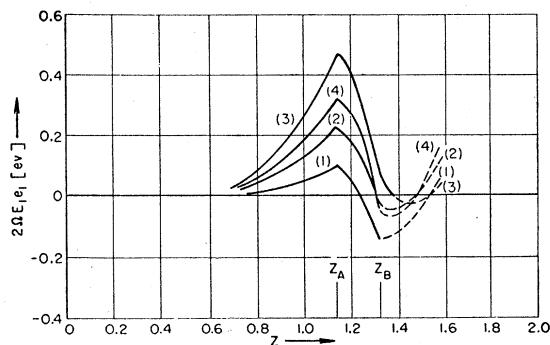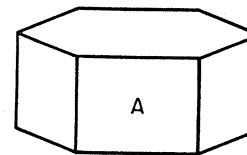

FIG. 11. First Brillouin zone for the h.c.p. lattice after Brillouin and Seitz.

with increasing z. The resulting relief in the rate of increase of the repulsive forces between the two surfaces with increasing z has been thought of as an effective partial pressure of the overlapping electrons to push the zone surface toward the center of the zone. Finally, if a zone surface is completely overlapped, there is no interaction between the two surfaces.

The Brillouin zones for two hexagonal lattices were considered, and it was shown how the forces of interaction between the Fermi and energy discontinuity surfaces could qualitatively explain the observed variations of the axial ratio from the ideal value for the close packing of spheres. A semiquantitative calculation for the axial ratio variation in cobalt and lithium indicate that the interactive forces under consideration are of sufficient magnitude to cause the distortions which are observed in these lattices.

Finally, it was shown that the Brillouin zone structure for the cubic crystals have such a symmetry that the "electron energy anisotropy" effect can be only of second-order magnitude. This would explain why the variations of the axial ratio with electron-atom ratio is peculiar to noncubic crystals.

APPENDIX I

In Fig. 3 is shown the first Brillouin zone for the h.c.p. lattice. Brillouin[18] and Seitz,[19] on the other hand, have taken the zone of Fig. 11 to be the first Brillouin zone for the h.c.p. lattice. In order to investigate which of these two is the correct zone, it is first noted that the h.c.p. lattice is made up of four interpenetrating orthorhombic lattices with unit vectors $A_1 = a$, $A_2 = \sqrt{3}a$, $A_3 = c$. Since the h.c.p. lattice, with two atoms α and β in the unit cell, consists of two simple hexagonal lattices with corresponding atoms at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{6}, \frac{1}{2})$, the potential at any point $\mathbf{r}$ may be expanded as the Fourier series

$$V = V_0 + \sum_s V_s e^{2\pi i \mathbf{k}_s \cdot \mathbf{r}},$$

where $\mathbf{k}_s$ is a vector denoting one of the points of the

FIG. 10. Initial electron energy change per atom with strain in h.c.p. lattice for distortion to $c/a < 1.633$ for an A face energy discontinuity of (1) 0.62 ev with $a = 3\text{A}$; (2) 1.0 ev with $a = 3\text{A}$; (3) 1.6 ev with $a = 3A$; and (4) 1.6 ev with $a = 2.5\text{A}$, when $Q_A : Q_B : Q_C = 1 : 1.6 : 1.2$.

[18] L. Brillouin, *Wave Propagation in Periodic Structures* (McGraw-Hill Book Company, Inc., New York, 1946).

[19] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

reciprocal lattice such that $\mathbf{k}_s \cdot \mathbf{r} = (s_1/A_1)x + (s_2/A_2)y + (s_3/A_3)z$ and the Fourier coefficient of the potential may be written

$$V_s = V_{s\alpha} + V_{s\beta}e^{\pi i(s_1 + \frac{1}{3}s_2 + s_3)},$$

where, since each of the simple lattices is described by $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$,

$$V_{s\alpha, \beta} = A_{\alpha, \beta}\{1 + e^{\pi i(s_1 + s_2)}\}.$$

According to the well-known degenerate perturbation calculation,[14] the magnitude of the energy discontinuity across the planes defined by

$$\mathbf{k}_s \cdot \mathbf{k} + \frac{1}{2}|k_s|^2 = 0$$

is given by $2|V_s|$. Therefore, if

$$V_s = 2A_\alpha \cos^2\frac{\pi}{2}(s_1 + s_2)\left\{1 + \frac{A_\beta}{A_\alpha}e^{\pi i(s_1 + \frac{1}{3}s_2 + s_3)}\right\} \quad \text{(i)}$$

vanishes for a given (s_1, s_2, s_3), there can be no energy discontinuity corresponding to this set of integers. In Fig. 4 is shown the second Brillouin zone for the h.c.p. lattice. A comparison of Fig. 11 and Fig. 4 with the zone
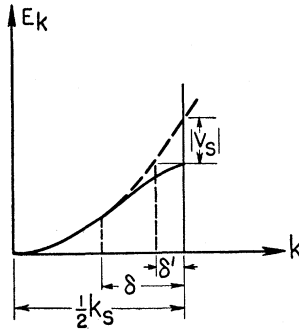

FIG. 12. Geometric relation between $|V_s|$ and δ.

of Fig. 3 reveals at once that the zone of Fig. 3 is what one would obtain if the Fourier coefficient for the surfaces $\{000, 1\}$ vanish whereas Fig. 11 is the zone one would obtain if this Fourier coefficient does not vanish. According to Eq. (i),

$$V_{001} = 2A_\alpha\{1 - A_\beta/A_\alpha\}. \quad \text{(ii)}$$

Mott and Jones[20] assume that the scattering coefficients A_α and A_β of the two atoms in the unit cell are identical and therefore take $V_{001} = 0$. Brillouin, on the other hand, has pointed out that the atomic potential about atom α by which the valence electrons are scattered is a planar reflection of the atomic potential about atom β. For an appropriate choice of axis, therefore, $V_\beta(x, y, z)$

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[20] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936), Chap. V.

$= V_\alpha(x, -y, z)$, so that for the $\{000, 1\}$ planes

$$\frac{A_\beta}{A_\alpha} = \frac{\displaystyle\int\int\int_{-\infty}^{\infty} e^{-2\pi i k_s \cdot \mathbf{r}}[V_\beta(x, y, z) - V_0]dxdydz}{\displaystyle\int\int\int_{-\infty}^{\infty} e^{-2\pi i k_s \cdot \mathbf{r}}[V_\alpha(x, y, z) - V_0]dxdydz},$$

$$= \frac{\displaystyle\int\int\int_{-\infty}^{\infty} e^{-2\pi iz/c}[V_\alpha(x, -y, z) - V_0]dxdydz}{\displaystyle\int\int\int_{-\infty}^{\infty} e^{-2\pi iz/c}[V_\alpha(x, y, z) - V_0]dxdydz}. \quad \text{(iii)}$$

If $y' = -y$ is substituted into the numerator of Eq. (iii), however, it is at once apparent that $A_\beta = A_\alpha$ and therefore that $V_{001} = 0$. Figure 3 should, therefore, be the correct first Brillouin zone for the h.c.p. lattice.

APPENDIX II

In the calculation of the parameters α and β, a simplified model is used in which it is assumed that (1) the Fermi surface is spherical except when it intersects a Brillouin zone boundary, (2) the electrons which contribute appreciably to the "electron energy anisotropy" effect are included within the solid angle formed by a rotation of a 30° plane angle about the k-vectors to the center of the respective faces (i.e., $\lambda = \sqrt{3}/2$), (3) the magnitude of the energy gap remains constant during a movement of any energy discontinuity surface, and (4) the energy discontinuity is constant over the discontinuity surfaces. In order to justify the 30° angle of rotation of assumption (2), it is necessary to estimate δ, the largest distance in k space from the Fermi surface to the energy discontinuity surface at which the electron energy is appreciably affected by movements of the discontinuity surface. Although all of the valence electron energies are affected by the movement of each face, nevertheless it will be sufficient to consider only those electrons whose wave numbers lie in a region of k space near to the moving face as contributing appreciably to the "electron energy anisotropy" effect. It should be noted that cobalt, which is assumed to have 0.7 valence electrons per atom, is h.c.p. with $c/a = 1.623$ while the h.c.p. form of nickel, with 0.6 valence electrons per atom, shows practically no distortion. It appears, therefore, that when the h.c.p. lattice has 0.7 electrons per atom, the Fermi surface is just close enough for movements of the Brillouin zone surfaces to appreciably affect the electron energies. Since the Fermi surface is approximated by a sphere, $z = 2\Omega \cdot (4\pi/3)k_0^3$, where Ω is the

atomic volume, and the radius of the Fermi sphere, when $z=0.7$, is $k_0=0.491/a$. Since $\frac{1}{2}k_s(A)=0.578/a$ is the distance from the center of the zone to an A face, $\delta=0.087/a$. If, therefore, the Fermi surface is just touching an A face, the critical plane angle is given by $\theta=\cos^{-1}[1-2/k_s(A)]=31°$. To avoid an overlap of solid angles for the different zone faces for the h.c.p. lattice, the value $\theta=30°$ is taken. The approximation $\lambda=\sqrt{3}/2$ becomes increasingly poor as the Fermi surface intersects more and more of the Brillouin zone surface.

The geometric correlation between δ and $|V_s|$ can be seen from Fig. 12. Geometrically,

$$\frac{|V_s|}{\delta'}=\left[\frac{d(h^2k^2/2m)}{dk}\right]_{k_s/2}=\frac{2E_k{}^f(\frac{1}{2}k_s)}{\frac{1}{2}k_s},$$

$$Q=\frac{|V_s|}{2E_k{}^f(\frac{1}{2}k_s)}=\frac{\delta'}{\frac{1}{2}k_s}.$$

If $\delta'=\frac{1}{3}\delta$, then $Q_A=0.05$, which is the value taken for Q in the calculations of Fig. 9. This means that all the electrons whose k vectors lie within a distance $3\delta'$ of the zone surface are considered in the estimation of the "electron energy anisotropy" effect. Geometrically, it appears reasonable that all the electrons which contribute appreciably to this effect have k vectors in this volume of k space.

Assumption (3) is employed in the evaluation of the term $z\langle\partial E_k/\partial e\rangle$ of $\partial U/\partial e$. Since $\langle\partial E_k/\partial e\rangle=0$ if there is no energy discontinuity, the term $z\langle\partial E_k/\partial e\rangle$ can be expressed as a series of terms to the first and higher powers of the energy discontinuity $2|V_s|$. From Eq. (4), a change in magnitude of the energy discontinuity with distortion is proportional to the strains. Any contribution to $\langle z\delta E_k\rangle$ due to a change in the magnitude of the energy gap with distortion will, therefore, be only of second order in the strains.

From the energy equation of the degenerate perturbation calculations in which the potential for the free electrons is expressed as

$$V(r)=V_0+\sum_s V_s e^{2\pi i \mathbf{k}_s \cdot \mathbf{r}},$$

the kinetic energy of an electron of wave number k is given by[14]

$$E_k=\frac{h^2}{2m}(k^2+\mathbf{k}\cdot\mathbf{k}_s+\frac{1}{2}k_s{}^2)$$
$$-\frac{1}{2}\frac{h^2}{2m}\{[k_s{}^2+2(\mathbf{k}\cdot\mathbf{k}_s)]^2+4(2m/h^2)^2|V_s|^2\}^{\frac{1}{2}}.$$

This expression is used in Eq. (1) for the evaluation of $\partial U/\partial e$.

APPENDIX III

Jones[21] has recently measured the lattice parameters for the ζ-phase of the silver-zinc system with $z=1.5$.

He finds $c=2.816$A and $a=7.639$A, with nine atoms to the unit cell. This is in agreement with recent measurements by Edmunds and Qurashi,[22] who found $c=2.8197$A and $a=7.6360$A. Jones found a first strong doublet corresponding to the Miller indices $(1, 1, 1)$ and $(0, 3, 0)$. From these figures the Fermi surface, after account is taken of intersection with the B faces, has a radius $k_0=0.226$A^{-1} while the B faces are found at $k_B=0.220$A^{-1} and the A faces at $k_A=0.227$A^{-1}. The probabel Brillouin zone would be as shown in Fig. 13. The decrease in the axial ratio as z varies from 1.46 to 1.5 would be due to an increasing repulsive force between the Fermi surface and the B faces where the two surfaces intersect and an increasing attractive force on the A faces which are not yet reached.

APPENDIX IV

Although there is no distortion to tetragonality in cubic crystals as a result of the "electron energy anisotropy" effect, nevertheless the interactive forces between the Fermi and zone surfaces exist. They are just those forces which Jones[23] has suggested are re-
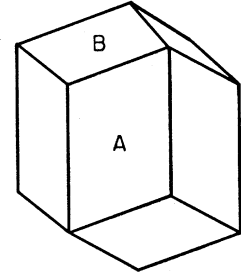

FIG. 13. Probable first Brillouin zone of silver-zinc ζ-phase after measurements of R. Jones.

sponsible for the Hume-Rothery[24] electron-atom ratio rules for phase changes in binary substitutional alloys. It should, therefore, be instructive to estimate the ratio of the Fermi energies for the f.c.c. and b.c.c. structures.

The total valence electron energy referred to the lowest electron energy state is the Fermi energy. If there is but one pair of zone faces separated a distance k_s in wave number space, and if the Fermi surface is approximated by a sphere, or portions of a sphere, then the Fermi energy is given by

$$U=2\Omega 4\pi\left\{\int_0^\mu\int_0^{k.}E_k k^2 dk d(\cos\theta)\right.$$
$$\left.+\int_\mu^1\int_0^{k_s/2\cos\theta}E_k k^2 dk d(\cos\theta)\right\}=\beta_k U_0, \quad \text{(i)}$$

[21] Richard Jones (private communication).

[22] E. A. Edmunds and Qurashi (private communication to R. Jones by H. Lipsom).
[23] H. Jones, Proc. Roy. Soc. (London) 144, 225 (1934); 147, 396 (1934). N. F. Mott and H. Jones, p. 170 of reference 20.
[24] W. Hume-Rothery, J. Inst. Metals 35, 295 (1926); The Metallic State (Oxford University Press, London, 1931), p. 328.
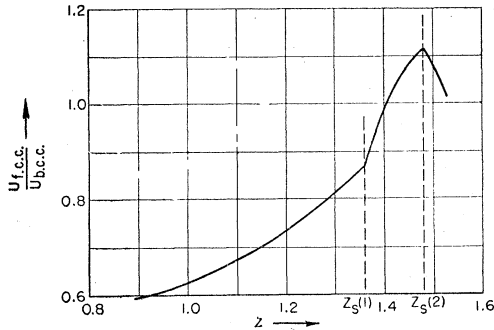
FIG. 14. Ratio of Fermi energies for a f.c.c. and b.c.c. lattice calculated from Eq. (v) with $Q_1=Q_2=0.05$.

where $U_0=\frac{3}{5}zE_k{}^f(k)$, $z=2\Omega\cdot(4\pi/3)k^3$, and $\beta_k=(k_s/2k)^5$ $\cdot f(\mu, Q)$ is a dimensionless parameter.

The volume enclosed by the Fermi surface in wave number space, Ω_k, can always be expressed as

$$\Omega_k=\alpha_k\cdot(4\pi/3)(k_s/2)^3, \qquad (ii)$$

where α_k is a dimensionless parameter. Since the electron-atom ratio z is conserved in a phase transformation,

$$(k_s/2k)^3=1/\alpha_k=z_s/z,$$

where $z_s=2\Omega\cdot(4\pi/3)(k_s/2)^3$. Since $\alpha_k=\alpha_k(\mu, Q)$ and z_s is known, there is the functional relation between z and μ for any given phase

$$z=\alpha_k(\mu, Q)\cdot z_s. \qquad (iii)$$

For a single pair of faces

$$\Delta U=U-U_0=U_0(\beta_k-1).$$

In the f.c.c. lattice there are four pair of nearest zone faces, and in the b.c.c. lattice six pair of zone faces. If the influence of the six small next-nearest zone faces of the f.c.c. lattice is neglected, and if the influence of each zone face is assumed to be that of an infinite plane, then

$$U_{\text{f.c.c.}}=U_0+4\Delta U=U_0(4\beta_k-3),$$
$$U_{\text{b.c.c.}}=U_0+6\Delta U=U_0(6\beta_k-5),$$

and

$$U_{\text{f.c.c.}}/U_{\text{b.c.c.}}=[4\beta_k(1)-3]/[6\beta_k(2)-5], \qquad (iv)$$

where $\beta_k(1)$ refers to the f.c.c. lattice and $\beta_k(2)$ refers to the b.c.c. lattice.

For the simple model of a spherical Fermi surface, it is readily shown that

$$\alpha_k(1)=(6\mu^{-2}-3\mu^{-3}-2), \quad \alpha_k(2)=(9\mu^{-2}-5\mu^{-3}-3).$$

If the constants Q_1 and Q_2 are taken for a measure of the energy gaps across the f.c.c. and b.c.c. zone faces respectively, then the respective values $\mu_1(z)$ and $\mu_2(z)$ for a given value of z can be calculated from relation (iii). Since $z_s(1)=1.362$ and $z_s(2)=1.480$, relation (iv) can then be written as

$$\frac{U_{\text{f.c.c.}}}{U_{\text{b.c.c.}}}=\frac{4(1.362/z)^{5/3}\cdot f(\mu_1(z), Q_1)-3}{6(1.480/z)^{5/3}\cdot f(\mu_2(z), Q_2)-5}. \qquad (v)$$

Figure 14 shows a plot of $U_{\text{f.c.c.}}/U_{\text{b.c.c.}}$ vs z for $Q_1=Q_2=0.05$. The perturbation value for E_k given in Sec. IV was used in the calculation of β_k to give

$$f(\mu, Q)\cong\begin{cases}\mu^{-4}-5Q^2\mu^{-2}\left[\frac{1}{4}\log\left(\frac{2}{Q}\right)-\frac{1}{3}\right] \text{ for } \mu\geq 1 \\[2ex] \frac{1}{4}(5\mu^{-4}-1)+5Q^2\left[\left(5-3\log\left(\frac{2}{Q}\right)\right)\frac{\mu^{-2}}{6} \right. \\[2ex] \left. +\frac{1}{2}\left(\log\left(\frac{2}{Q}\right)-1\right)\right] \text{ for } \mu\leq 1.\end{cases}$$

This calculation shows that if the Fermi energy alone is used as a criterion for the relative stability of the f.c.c. and b.c.c. phases in a metal alloy, the f.c.c. phase has the lower Fermi energy and therefore is the more stable for $z<1.4$. For larger values of z, however, there is a range in which the b.c.c. phase is the more stable. This range corresponds to the β-phase region in the β-brasses.